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Influence of Thermal and Gamma Radiation on Electrical Properties of Thin NiO Films Formed by RF Sputtering

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Abstract

Electrical properties of p-NiO films fabricated by RF magnetron sputtering were characterized after deposition, heat treatment in oxygen or argon and after irradiation using 660 keV photons. The results show, that resistivity of the NiO film is strongly increased after thermal processes in Ar and gradually increased after subsequent irradiation processes because of the decrease of holes concentration.

Keywords: Nickel oxide; thin films; transparent semiconductor; gamma radiation.

1. Introduction

Nickel oxide is an interesting material due to its semitransparent, semiconducting, thermoelectric and catalytic properties [1–3]. It is characterized by a direct band gap of about 4 eV and a possible wide range of resistivity dependent on the growth method. Some of potential applications of NiO films in electronic devices like gas sensors, counter electrodes, displays, LEDs or variable reflectance mirrors require well controlled electrical parameters and stable ohmic contacts. Although chemical inertness of NiO compound is well known, electronic parameters of NiO films are vulnerable to environment, especially at elevated temperature. We examined electrical properties of NiO films after sputtering deposition and thermal treatment in neutral and oxidising environment. Some NiO structures were exposed to gamma radiation to disclose capability of this semiconductor in sensor application considered in papers [4]. The measurements concern resistivity, hole concentration, mobility, ohmic contact resistance and impedance.

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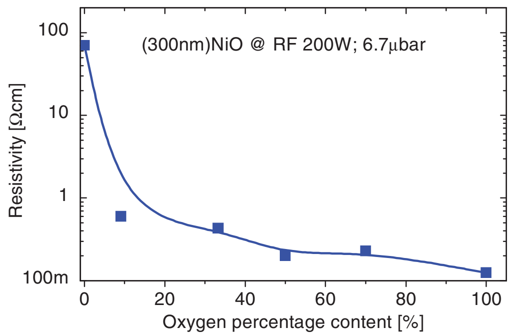
2. Experimental

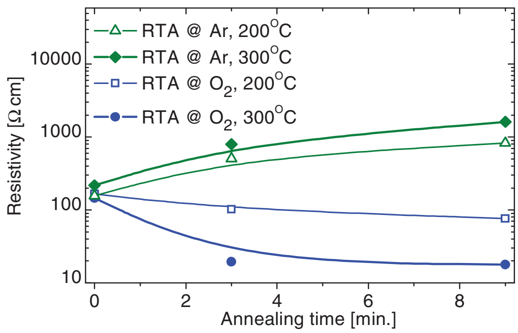
Thin films were deposited by RF magnetron sputtering from 3"NiO target (99.99% purity) in O_2/Ar plasma (99.9999% purity gases) onto n-Si(001) and quartz substrates at power P_{RF} of 150 W or 200 W, controlled temperature from room temperature (RT) up to 500°C. Morphology and structural properties of the films were characterized using Scanning Electron Microscopy (SEM) and X-Ray diffraction. The compositions of the films were estimated by Energy Dispersive Analysis of X-rays (EDAX). Electrical parameters were obtained from Hall measurements in van der Pauw geometry and capacitance-voltage (C-V) measurements of n-Si/p-NiO junction. A n-Si/p-NiO junction diode with 300 nm thick NiO film was fabricated using n-Si ($n = 8\cdot 10^{15}$ cm^{-3}) samples with Ti-silicides ohmic contact on the backside of Si formed before NiO deposition. A pattern of NiO circles with 1 mm diameter was fabricated using photolithography. (200 nm)Au top contact layer was deposited by sputtering and lift off technique to form ohmic contact to NiO films. NiO conductivity and contact resistance were measured using Circular Transmission Line Method (cTLM). NiO samples were thermally treated by tungsten lamps radiation using the Rapid Thermal Annealing system and ambient of Ar or O_2 at the temperature controlled by thermocouple. The diode structures were exposed to gamma radiation using ^{137}Ce source of 660 keV energy at dose rate of 11.4 µGy/s. The structures were characterized using C-V and Nyquist plots.

3. Results and discussion

Resistivity of deposited NiO films vs. oxygen content during sputtering is presented in Fig. 1a. Increase in oxygen content in gas mixture results in decrease of sheet resistance at constant film thickness. This result is complies with ones obtained by Hotový et al. [5]. Hall measurements confirm p-type conductivity of these films. Such high sheet resistance is associated with low hole mobility in range of 0.02 - 0.8 cm^2/Vs for films deposited at room temperature. In the case of sputtering only in Ar, the film resistance is sometimes extremely high - sheet resistance of about 4 GΩ/sq. is observed for the NiO film deposited at 150 W. Moreover, negative Hall voltage signal indicated n-type conductivity has been observed occasionally suggesting high level of minor carriers. Increase of oxygen amount in the sputtering gas mixture results in increase of holes' concentration to level of 10^{20} cm^{-3}. These results are consistent with the model of p-type conduction in NiO for composition ratio O/Ni exceeding 1 and confirmed by EDX measurements of the ratio to be $1.1<O/Ni<1.26$ for our p-type films. Following this idea a post-deposition annealing of highly resistive NiO films in oxygen results in decrease of resistivity, as it can be seen in Fig.1b. Resistivity of NiO samples annealed in Ar increases rapidly with annealing time. This effect might be caused by release of oxygen as it was observed at temperature above 263°C [2]



(a)



(b)

Fig. 1. (a) Resistivity of NiO film vs. oxygen percentage content in sputtering deposition at RT, RF power P_{RF}=200 W. (b) Resistivity after RTA processing in Ar or in O_2 for (300 nm)NiO film deposited at RT, P_{RF}=150 W.

and also suggested by our EDAX measurements. XRD study of deposited NiO films revealed fcc structure of polycrystalline grains with texture dependent on oxygen content in plasma and temperature – <111> texture for deposition in Ar and <200> texture for deposition in O_2. Calculation of NiO lattice parameter revealed lattice constant increased from 4.194 Å to 4.303 Å for films deposited at oxygen content in gas mixture from 9% to 50%, respectively. These values are above lattice constant of 4.1771 Å characterizing bulk material. After annealing the films at 300°C or above, the constant is decreased.

It can be seen in table 1, that annealing at 300°C resulted in an increase both carrier mobility and resistivity of the films. Thermal processing at 350°C caused a rise in resistivity by factor of 30. Carrier concentration was lower after each one of the mentioned thermal processes. Annealing in O_2 at 400°C can reduce carrier concentration to the level of $1{\cdot}10^{14}$ cm^{-3} and raise resistivity to 600 Ωcm. Moreover, we observed that applying (150 nm)SiO_2 capping layer on top of NiO film stabilizes its electrical parameters when they are stored in air. It was confirmed on cTLM structure with (300 nm) NiO film deposited at P_{RF} = 200 W, RT, F_{O2} = 20% and next sealed from air by PECVD deposition of (150 nm)SiO_2 film. Contact resistivity of $2{\cdot}10^{-3}$Ωcm^2 is unchanged after a few months' storage. Film conductivity as well as specific contact resistance are repetitive functions vs. temperature for annealing in air up to 250°C. Assuming that holes are thermally created, activation energy of 140 eV was calculated. Decreasing contact resistivity with an increase of temperature can be explained by suggestion of correlated increase of p-concentration.

Table 1. Electrical parameters of NiO films deposited at RT, P_{RF}=200 W, oxygen content $F_{O2} = p_{O2}/(p_{O2} + p_{Ar})$, as well as after RTA in oxygen at 300°C and 350 °C for 1 hour; p_X - partial gas pressure, p - hole concentration, μ - carrier mobility and ρ - resistivity.

no	F_{O2}	as-deposited			RTA at 300°C			RTA at 350°C		
	[%]	p [1/cm^{-3}]	μ [cm^2/V·s]	ρ [Ωcm]	p [1/cm^{-3}]	μ [cm^2/V·s]	ρ [Ωcm]	p [1/cm^{-3}]	μ [cm^2/V·s]	ρ [Ωcm]
1	9	$5{\cdot}10^{19}$	0.2	0.6	$1{\cdot}10^{19}$	2	0.3	-	-	-
2	20	$1.5{\cdot}10^{20}$	0.20	0.43	-	-	-	$3.5{\cdot}10^{18}$	0.21	13
3	34	$1{\cdot}10^{20}$	0.15	0.2	$7{\cdot}10^{19}$	0.2	1.6	-	-	-
4	100	$2{\cdot}10^{20}$	0.36	0.12	$3{\cdot}10^{19}$	0.5	2	-	-	-

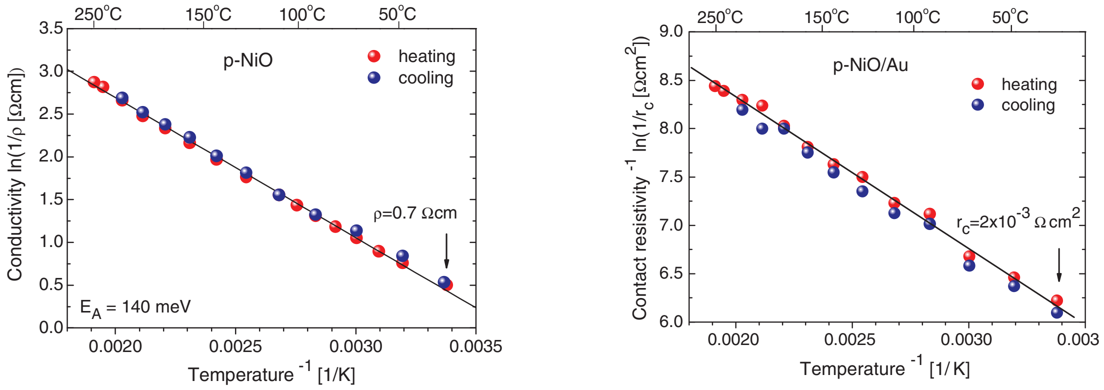
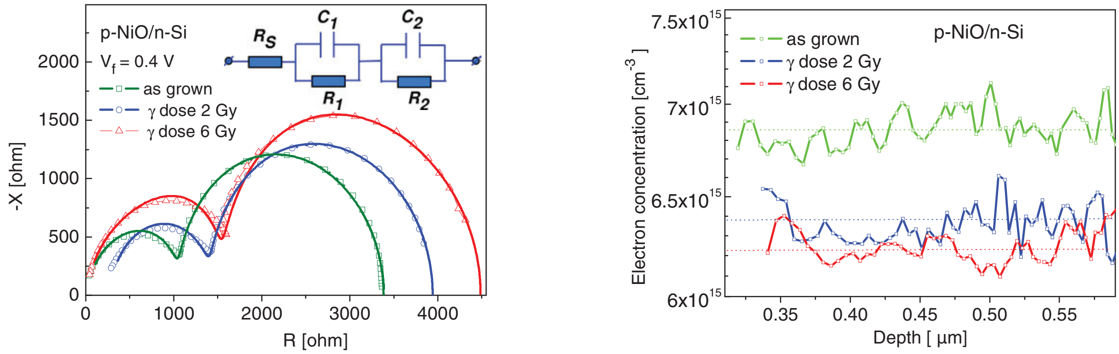


Fig. 2. (a) NiO conductivity (1/ρ) versus temperature measured on cTLM structure with (300 nm)NiO film deposited at RT, P_{RF}=200 W, oxygen content F_{O2} = 20% and NiO surface sealed from air by (150 nm)SiO_2 film as well as (b) contact resistivity.

Research on electrical properties of p-NiO film after γ irradiations was performed by impedance measuring on the p-n diodes at frequency from 0.5 kHz to 2 MHz. The results in the form of Nyquist plots at forward bias V_f = 0.4 V are shown in Fig. 3a. The impedance functions Z(ω) = R(ω)-iX(ω) are simulated using the model of three RC impedances, where R_1C_1 is correlated with diffusion capacity,

R_2C_2 is associated with NiO film impedance and R_s is a series resistance. For a sequence of γ irradiations with dose of 2 Gy and 6 Gy the calculations show unchanged diffusion capacity C_1= 22.2 nF and R_1 increased from 2.4 kΩ to 2.57 kΩ and to 3.06 kΩ, but impedance of NiO film is increased after the irradiations from 1.05 kΩ to 1.17 kΩ and to 1.62 kΩ at capacity C_1 of 516 pF, 464 pF and 448 pF, respectively. These results are in good agreement with carrier concentration of p-NiO calculated from p-n heterojunction [6]. Electron concentration of n_{Si}^* at the junction is shown in Fig. 3b. The hole concentration of NiO is decreased from $4.36 \cdot 10^{16}$ cm^{-3} to $3.0 \cdot 10^{16} cm^{-3}$ and $2.86 \cdot 10^{16} cm^{-3}$ after γ irradiation with doses of 2 Gy and 6 Gy, respectively.



(a) (b)

Fig. 3. (a) Nyquist plots measured at frequency from 0.5 kHz to 2 MHz on p-NiO/n-Si diode before and after γ irradiation using ^{137}Ce source. (b) Electron concentration n^*_{Si} in Si vs. the junction depth calculated from the C-V plots for the p-NiO/n-Si diodes.

4. Conclusions

Electrical parameters of highly conductive NiO films are susceptible to air exposure for time of a few weeks, so masking layers like 150 nm thick SiO_2 film are required to ensure long term stable electrical functionality of the film. Thermal irradiation of NiO films in O_2 at temperature of 300^{o}C improves carrier mobility. Measurement of n-Si/p-NiO junction exposed to γ radiation for a low dose of 2 Gy showed increased real and imaginary parts of the NiO impedance, what can be explained by decrease in holes concentration calculated from C-V characteristics. Resistivity is higher after following γ irradiations.

5. Acknowledgements

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